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by

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## PHOTOREFRACTIVITY IN DOPED NONLINEAR ORGANIC POLYMERS

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# Photorefractivity in doped nonlinear organic polymers

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## ABSTRACT

This paper describes the properties of a new class of materials exhibiting the photorefractive effect, doped nonlinear organic polymers. Photorefraction (at 647.1 nm) was established by a combination of hologram erasability, correlation with photoconductivity and electro-optic response, and enhancement by external fields in numerous samples (178 to 533  $\mu\text{m}$  thick) of two nonlinear epoxy materials doped with hole transport agents based on p-diethylaminobenzaldehyde-diphenyl hydrazone (DEH). Diffraction efficiencies up to 0.1% were observed at bias fields near 100 kV/cm. A useful property of these materials is that poling of the nonlinear chromophores is partially reversible, permitting partial control of the grating readout independent of the space-charge field formed. The polarization anisotropy of grating readout is consistent with the photorefractive mechanism. Two-beam coupling measurements of both absorption and index gratings show (i) the absorption gratings are  $\approx 10$  times smaller than the index gratings, and (ii) the phase shift of the index grating is near  $90^\circ$ , which cannot occur via photochromism, heating, or any other process except photorefractivity.

## 1. INTRODUCTION

The photorefractive (PR) effect occurs in certain materials which both photoconduct and show second-order optical nonlinearity (Figure 1). The effect arises when charge carriers, photoexcited by a spatially modulated light intensity, separate and become trapped to produce a nonuniform space charge distribution. The resulting space-charge field then modulates the refractive index via the electro-optic effect to create a phase grating which can diffract a light beam. The ingredients necessary for producing a PR phase hologram are therefore: photoionizable charge generator, transporting medium, trapping sites, and dependence of the index of refraction upon space-charge field. Since the first observations of this effect in  $\text{LiNbO}_3$  in 1967<sup>1</sup>, many detailed theoretical and experimental studies of the effect have occurred,<sup>2</sup> and a variety of novel applications have been proposed, including high density optical data storage, many image processing techniques, phase conjugation, beam fanning limiters, simulations of neural networks and associative memories, and programmable interconnection.

The PR effect, as defined, is distinct from the many other possible mechanisms of forming gratings in optical materials, such as photochromism, thermochromism, heating, excited states, conventional  $\chi^{(2)}$ , and so forth<sup>3</sup>. In any report claiming photorefraction in a new material, the dominance of the PR process over these many other processes must be conclusively proven. This is

crucial, because many of the novel applications of photorefractives<sup>4</sup> follow from the nonzero grating phase shift and the nonlocal nature of the interaction of the material with the light beam.

Until very recently, all materials showing the PR effect have been inorganic crystals<sup>2</sup>. For inorganic crystals, it is well-known that the diffraction figure-of-merit  $n^3 r_{\text{eff}} / \epsilon$  (where  $n$  is the optical index,  $r_{\text{eff}}$  is the effective electro-optic coefficient, and  $\epsilon$  is the dc dielectric constant) does not vary much from material to material, which is a result of the fact that the optical nonlinearity is driven chiefly by the large ionic polarizability. For organic nonlinear materials, however, large electro-optic coefficients are not accompanied by large DC dielectric constants, thus a potential improvement in performance of up to a factor of ten is possible with organic photorefractives<sup>5</sup>.

Recently, the PR effect was observed in a carefully grown nonlinear organic crystal COANP doped with TCNQ<sup>6,7</sup>. The growth of high-quality doped organic crystals, however, is a very difficult process because most dopants are expelled during the crystal preparation. Polymeric materials, on the other hand, can be doped with various molecules of quite different sizes with relative ease. Further, polymers may be formed into a variety of thin-film and waveguide configurations as required by the application. A report of a photoconducting electro-optic polymer film with impressive photoconductivity has appeared<sup>8</sup>, but no PR gratings were reported.

The first polymeric photorefractive material<sup>5,9</sup> was composed of the nonlinear epoxy polymer bisphenol-A-diglycidylether 4-nitro-1,2-phenylenediamine (BisA-NPIA)<sup>10</sup> made photoconductive by doping with the hole transport agent diethylamino-benzaldehyde diphenylhydrazone (DEH). This paper summarizes the properties of this material and several other combinations of nonlinear polymers and charge transport agents that we have found to show the PR effect using a combination of measurements of photoconductivity, nonlinearity, holographic grating formation, polarization anisotropy, and two-beam coupling phase measurements. Here we have chosen to use polymers which contain covalently bound nonlinear chromophores, and to dope them with small-molecule transport agents. Second-order nonlinearity is achieved by poling, i.e., by aligning the nonlinear chromophores in an electric field. Thus the polymer provides both the charge generation and the second-order nonlinearity; charge transport occurs via the dopant molecules; suitable trapping sites, although not deliberately added, turn out to be sufficiently abundant in this particular amorphous medium.

It should be noted that transport molecule doping of a non-linear polymer is not the only conceivable approach to the formulation of a PR polymer. One might instead dope a charge transporting polymer such as poly(phenylene vinylene) with a non-linear small molecule, or both species might be made part of the polymer structure. In addition, the PR response might be optimized by addition of a more efficient charge generating dye or pigment (sensitizing agent<sup>11</sup>) and/or specific trapping sites for the charge carriers. Another approach already familiar from work on inorganics<sup>12</sup> would be to utilize a  $\chi^{(n)}$  polymer in an electric field to produce the optical nonlinearity<sup>13</sup>. In a fully optimized material, all four of the required functionalities can be attached to the polymer backbone. Our early attempts to achieve the PR effect did employ all four ingredients, but since only two are sufficient, this work concentrates on a more complete characterization of the simpler system containing only the nonlinear polymer and the charge transporting agent.

## 2. MATERIALS

This paper reports results on four combinations of two different nonlinear polymers and three hole transport agents. The polymers (see Fig. 2) are diglycidyl ether derivatives of bis-phenol-A or nitroaniline partially crosslinked with nonlinear chromophores which are nitroaniline derivatives. The molecular dopants are hydrazones, which because of their low oxidation potentials and extended  $\pi$ -electron systems, are hole transport agents.

Most of the data reported in this paper refer to the combination bisA-NPDA/DEH, although the properties of the other combinations will be summarized in tabular form. The component materials were dissolved in propylene glycol monomethyl ether (or its acetate) in various weight ratios and films cast by either spin or draw-bar coating techniques. For the thick (several hundred micron) films required for demonstration of grating formation, a special coating technique was used: the solution was fed drop-wise onto two heated ITO-glass slides, with partial drying between drops, and dried and cured further for 30 minutes at 95° C when sufficient material had accumulated. Then the two glass slides were pressed together to form a sandwich structure with transparent electrodes on either side of the polymer. Crosslinking of the epoxy groups was deliberately limited by ensuring that the samples never exceeded 95° C. The partial curing and the presence of some residual solvent allows considerable molecular motion, and permits alignment of the nonlinear chromophores by an external field at room temperature. Thus, with sufficient waiting time, it was possible to switch on and off the electro-optic response.

### 3. PHOTOCONDUCTIVITY

Photoconductivity was measured by two different techniques. First, a conventional two-electrode sandwich sample was used to determine the dc conductivity change resulting from illumination with a dye or krypton laser<sup>9</sup>. Second, the rate of decay of a corona-deposited surface charge on a sample  $\approx 5 \mu\text{m}$  thick was measured<sup>15</sup>. This second xerographic method gives a much more accurate determination of the conductivity at low intensity, and eliminates the possibility of sample heating. There was no significant difference between the results from the two methods.

First of all, the photoconductivity increases linearly with light intensity, with exponent  $1.00 \pm 0.03$ . Second, the photoconductivity increases very rapidly with concentration of DEH, up to  $10^{-12} (\Omega - \text{cm})^{-1}$  per W/cm<sup>2</sup> at 30 weight %, and its spectral response follows the absorption spectrum of the NPDA chromophore. Therefore, we conclude that NPDA is acting as the charge generator, with transport occurring, as expected, via the DEH dopant molecules.

Figure 3 shows the photoconductive sensitivity ( $\sigma_{ph}/\text{intensity}$ ) of the bisA-NPDA/DEH material obtained by the xerographic discharge method<sup>15</sup>. Below 500 nm where the polymer allows light absorption in only the surface layer, negative charging requires electrons to move through the bulk of the sample to achieve discharge. The greatly increased photoconductive sensitivity for the opposite case, positive charging, proves that hole transport is much more efficient than electron transport, as expected.

### 4. SECOND-ORDER NONLINEARITY

The electro-optic coefficients of the samples were measured at low frequencies (10 - 10,000 Hz) using a standard Mach-Zehnder interferometer. The observed response was proportional to the

applied field  $E_0$  except for a small amount of hysteresis at fields below 5 kV/cm. Upon changing or reversing the applied field, the observed EO response grows nonexponentially, attaining in a matter of minutes approximately 90% of its long-time (i.e. many hours) value as the nonlinear chromophores are aligned. The slow time dependence of the observed EO response confirms that the source of the nonlinearity is molecular alignment rather than a Kerr effect. Separate measurement of the Kerr coefficient at twice the modulating frequency yielded the result that when the DC field is present, the Kerr contribution to our measurement of the electro-optic coefficient was on the order of one percent.

The right ordinate of Figure 4 shows the steady-state EO response of a 30 wt. % DEH mixture in bisA-NPDA at 632 nm. For each value of applied field, the chromophore orientation was allowed to equilibrate for  $\approx 5$  min. The measured EO coefficient (p-polarized, neglecting birefringence)  $r_{\text{meas}} = r_{33} \sin^2 \alpha + r_{13} \cos^2 \alpha$  is a linear combination of the longitudinal  $r_{33}$  and transverse  $r_{13} = r_{23}$  coefficients where the 3-direction is the direction of the applied electric field (normal to the film plane) and  $\alpha = 32.1^\circ$  (for  $n = 1.63$ ) is the angle of propagation within the film.

Though the data of Fig. 4 were measured on the same sample, considerable scatter in EO coefficients (25 %) was observed due to sample inhomogeneity. Separate measurements of sample thickness changes<sup>16</sup> revealed that the piezoelectric coefficient  $d_{33} \sim +0.2$  pm/V, which may contain a contribution from electrode attraction, also made a small (10-30 %) contribution to the observed EO measurements. The data in Fig. 4 are not corrected for these observations,

## 5. PHOTOREFRACTIVE GRATING FORMATION

Thus, three of four necessary ingredients for a PR material (absorption, transport, and EO response) can be easily measured in our polymer mixtures. The polymer would be expected to supply a large density of traps, which may be polymer chain ends or other defects, but there is no guarantee that these traps will be suitable for the formation of an erasable PR grating, or that other photochromic processes which would overwhelm a PR effect are not present. The dominance of the PR effect in our materials has been verified by field-dependent and polarization dependent volume holography<sup>9</sup> using the geometry of Figure 5. Two mutually coherent Gaussian "writing" beams at  $\lambda_v = 647.1$  nm with equal intensities of 13 W/cm<sup>2</sup> were intersected in the sample at incidence angles of  $30^\circ$  and  $60^\circ$  (in air), respectively, thus producing interference fringes with spacing  $\Lambda_x = 1.6$   $\mu\text{m}$  oriented  $25^\circ$  from the film plane. A third, much weaker, "reading" beam directed opposite to the  $60^\circ$  writing beam was Bragg diffracted from the grating formed by the writing beams. The diffraction efficiency  $\eta$  was recorded as the ratio of diffracted to incident reading beam power.

The influence of  $E_0$  on  $\eta$  is shown in Fig. 4, left scale, where at each point the molecular alignment was allowed to reach steady-state in the field for 10 min. The value of  $\eta = (n^3 r_{\text{meas}} \pi L G E_{\text{sc}} / 2 \lambda_v)^2$  increases rapidly with  $E_0$  through increases in both the PR space-charge field  $E_{\text{sc}}$  and the EO response  $n^3 r_{\text{meas}}$ , where  $L = 356$   $\mu\text{m}$  and  $G$  is a polarization and geometrical factor equal to 0.86. The PR space-charge field in the standard model<sup>2, 17</sup> is

$$E_{\text{sc}}^2 = \frac{I_d^2 + I_{\text{og}}^2}{(1+B)^2 + B^2 (E_{\text{og}}/E_d)^2} \quad (1)$$



where  $E_{\pi}$  is the component of  $E_0$  along the grating wavevector,  $E_0 = k_s k_n T / e = 1.0 \text{ kV/cm}$  and  $k_s = 2\pi/\Lambda_s = 3.9 \times 10^4 \text{ cm}^{-1}$ . The inset to Fig. 4 shows  $\eta$  divided by  $(n^3 r_{\text{eff}})^2$ , which should be proportional to  $E_{\pi}^2$ . The solid line is a least-squares fit to Eq. 1 with two adjustable parameters: an overall multiplicative factor of  $\approx 2.5$  and  $B = 0.034$  which yields the effective density of photorefractive traps  $N_{\text{pr}} = k_s^2 \epsilon \epsilon_0 k_n T / B e^2 = 1.9 \times 10^{15} \text{ cm}^{-3}$  ( $\epsilon = 2.9$ ). The fit provides a good description of the shape of the experimental data, even though one might expect that a more complicated model including geminate recombination or other details of the field dependence of charge generation and mobility might be required in this material<sup>18</sup>. The maximum  $E_{\pi}$  reached, at an applied field of 126 kV/cm, from Eq. 1 is 26 kV/cm, a value which is larger than is generally attainable in inorganic PR materials. Clearly, the low dielectric constant of the polymer allows a larger field for the small trapped charge density  $N_{\text{pr}}$  than might be possible in inorganics. The low values of  $\eta$ , on the other hand, are to be expected due to the short optical path lengths and relatively small EO coefficients of this particular polymer (see below).

To further establish that the observed gratings were indeed photorefractive in origin, we recorded gratings at large applied voltage, removed the writing beams, and observed the diffracted signal as the applied voltage was altered, with typical results shown in Fig. 6. From a to b, the grating was recorded for 2.5 min. in a field of -84.3 kV/cm which had been applied long in the past. The fluctuations in the signal as it rises to its steady-state value are due to slow changes in the optical paths of the writing beams. At b, both writing beams and the applied field were switched off resulting in a rapid decrease in the signal. We attribute this to initial relaxation of the chromophore alignment, without loss of the space-charge (except for the slow erasure by the much weaker reading beam), because the signal returns upon application of a field of either sign (c and d in Fig. 6). The dynamics for signal recovery are consistent with that required for reorientation of the nonlinear chromophores and are far slower than the charging time of the circuit, thus ruling out strong Kerr effect contributions. At e, one of the writing beams was turned back on to erase the space-charge field in a time of order 30 s, which should be compared with the dark lifetime of order 500 s, limited by the dark conductivity of the material. Thus, Fig. 6 establishes the relative independence of space-charge formation and erasure from the molecular alignment whose only purpose is to permit readout, and reinforces the interpretation in terms of a photorefractive mechanism. Further, we remark that an external field is required for the generation of a detectable diffraction grating; attempts to write a grating in zero field and then read out with a field applied produced no detectable signal. The gratings can be erased multiple times, most readily in an applied field with uniform illumination.

## 6. POLARIZATION ANISOTROPY

Further evidence for the PR mechanism may be obtained from the polarization anisotropy during readout. After writing with both beams p-polarized or both beams s-polarized, one may consider how the diffraction efficiency depends upon the polarization of the reading beam. For the general case of oblique readout from tilted PR phase gratings<sup>19</sup>,

$$\eta_s = \sin^2 \left[ \frac{\pi n^3 r_{13} E_{\text{sc}} d \sin \theta_g}{2 \lambda_v (\cos \alpha_0 \cos \theta_1)^{1/2}} \right] \quad (2)$$

$$\eta_p = \sin^2 \left[ \frac{\pi n^3 r_{\text{eff}}^p E_{\text{sc}} d \cos 2\theta_o}{2\lambda \sqrt{(\cos \alpha_o \cos \theta_1)^{1/2}}} \right] \quad (3)$$

with  $d$  the sample thickness,  $\theta_g$  the angle between the grating wavevector and the film plane,  $\theta_1$  the incidence angle for beam 1,  $\alpha_o$  the incidence angle for beam 2, and  $2\theta_o$  the full angle between beams 1 and 2, all in the material. The effective EO coefficient for p-polarized readout is

$$r_{\text{eff}}^p = r_{13} [\cos \theta_1 \sin(\alpha_o + \theta_g) + \sin \theta_1 \cos \alpha_o \cos \theta_g] + r_{33} \sin \theta_1 \sin \alpha_o \sin \theta_g \quad (4)$$

Using the standard estimate for weak poling with linear chromophores  $r_{33}/r_{13} = 3$ , the ratio  $\eta_p/\eta_s \sim 8.1$  for external incidence angles of  $30^\circ$  and  $60^\circ$ . We measure a polarization anisotropy of  $\sim 6 \pm 2$ , in reasonable agreement.

## 7. TWO-BEAM COUPLING AND GRATING PHASE MEASUREMENTS

Final conclusive evidence for the observation of the PR effect is provided by two-beam coupling measurements of the amplitude and phase of both the absorption and index gratings present after irradiation. While many methods have been proposed for PR grating phase measurements, the work of Sutter et al. is particularly useful<sup>7</sup>, and we follow their approach here. The experiment involves writing a grating with two equal-intensity writing beams with two detectors measuring the transmitted intensity of the writing beams. After grating formation, the sample itself is translated laterally, moving the absorption and index gratings present in the material across the interference pattern formed by the two writing beams in a time short compared to the writing time. The two diffracted beams interfere with the transmitted beams, providing a characteristic modulation of the power received at each detector. A key feature of this method is that while the diffraction efficiency of the grating may be  $10^{-4}$ , the amplitude variations of either beam are much larger,  $10^{-2}$ , since homodyne detection occurs automatically. The transmitted powers are given by

$$P_1 \sim 1 - 2\Lambda \cos(\phi_\Lambda + k_g x) - 2P \sin(\phi_p + k_g x) \quad (5)$$

$$P_2 \sim 1 - 2\Lambda \cos(\phi_\Lambda + k_g x) + 2P \sin(\phi_p + k_g x) \quad (6)$$

with  $\Lambda$ ,  $\phi_\Lambda$  the amplitude and phase of the absorption and  $P$ ,  $\phi_p$  the amplitude and phase of the index grating.

Measurements of this sort on bisA-NPDA/DEH<sup>20</sup> show that all gratings observed are predominantly index gratings. When measurable, the absorption grating is  $\sim 10$  times smaller than the phase grating. At high field, the phase of the index gratings approach  $\pi/2$  as would be expected from the standard photorefractive model<sup>21</sup>:

$$\text{phase}(E_{\text{sc}}) = \text{phase} \left[ \frac{m(E_o + iE_d)}{1 + E_d/E_q - iE_o/E_q} \right] \quad (7)$$

Using the value of  $B = E_d/E_q$  from Section 5, an estimate for the trap-limited space-charge field  $E_q \approx 29.4$  kV/cm may be derived. Figure 7 shows a plot of Eq. (7) (solid line) along with measurements of the index grating phase for a sample of bisA-NPDA/DEH. The data follow the general trend of Eq. (7) with an offset that may be due to the limitations inherent in applying the standard photorefractive model to this organic material. In any case, the observation of index gratings offset

by  $\approx 90^\circ$  conclusively verifies that the material is indeed photorefractive, as no other phenomenon can produce this nonlocal effect without the application of alternating electric fields.

## 8. GENERALITY AND HIGHER EFFICIENCY PHOTOREFRACTIVE POLYMERS

Preliminary results for several other material combinations are shown in Table 1 (30 samples). In each case, sample inhomogeneity and partial crosslinking contributed to the range of measured values.

Material Property	bisA-NPDA /DEH	bisA-NPDA /DEH	bisA-NPDA /DECH	NNDN -NAN/DEH
$\sigma_{ph}$ , units $10^{-12}$ ( $\Omega - cm$ ) $^{-1}$ / W / cm $^2$	0.06-12.0	0.02-0.7	0.33	0.2-2.8
$n^j r_{meas}$ (pm/V)	0.1-5	0.2-1	0.15-1.2	1.4-17
$\eta$	$5 \times 10^{-7}$ to $5 \times 10^{-5}$	$4 \times 10^{-6}$ to $10^{-5}$	$9 \times 10^{-6}$	$1.2 \times 10^{-5}$ to $1 \times 10^{-3}$
at field (kV/cm)	125	110	110	85

Table 1

Of particular interest is the polymer NNDN-NAN, which features a higher concentration of nonlinear moieties and hence a higher nonlinearity<sup>14</sup>. Figure 8 shows the dependence of the hologram diffraction efficiency upon applied electric field for NNDN-NAN/DEH. The curve is similar in shape but larger in magnitude compared to that for bisA-NPDA/DEH. It is clear from these results that a wide variety of polymeric photorefractive materials may be fabricated. However, as stated above, in each case it is necessary to prove that any gratings observed result from a true PR effect.

## 9. CONCLUSION

Several of the details of the PR mechanism must be different in these organic polymers than in the inorganic crystals studied most extensively to date<sup>2</sup>. Charge generation is expected to be highly field-dependent, and an Onsager<sup>18</sup> or other charge generation model must be considered for applicability. The mobility in these materials is relatively low (e.g., DEH in polycarbonate resin has a mobility of  $10^{-7}$  to  $10^{-6}$  cm $^2$ /Vs for this concentration range at room temperature<sup>22</sup>) and may set a limit to the speed of response, although other conjugated polymers can have quite high mobilities<sup>23</sup>. The properties of these materials can be enhanced by the addition of traps and/or charge-generation agents. Finally, we have taken advantage of the ability to turn the polarization on and off in a material with low glass transition temperature. The resulting dipolar relaxation process is highly dispersive. For most applications, it would be preferable to freeze in permanent polarization by fully curing the epoxy in the dark in the presence of an electric field<sup>10</sup> or by using other nonlinear polymer binders poled above a high glass transition temperature.

With the large variety of possible variations in composition of PR polymers that may be envisioned, the ultimate limitations of organic polymers as PR materials cannot be established at this time. Only by careful scientific study of the performance and of the microscopic mechanisms can the future utility of this new materials class be established. In any case, it is certainly clear that other examples of PR polymers will soon be forthcoming from many locations around the world.

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### The Photorefractive Effect

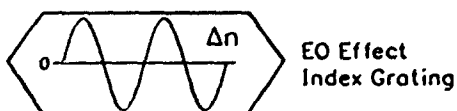
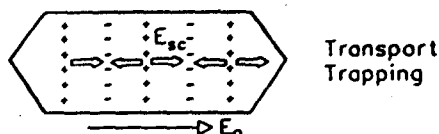
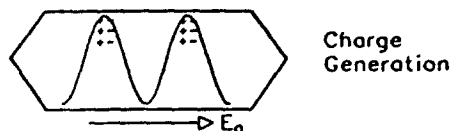
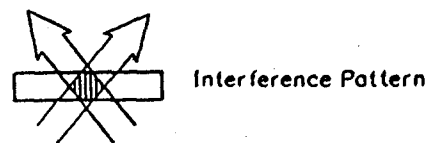


Fig. 1. Illustration of photorefractive grating formation.

Fig. 2. Polymers and transport molecules used in this work. The nonlinear polymers are (A) bisA-NPDA<sup>10</sup>, (B) NNDN-NAN<sup>14</sup>. Crosslinking occurs at the multifunctional amines. The transport molecules are (C) DEH, (D), DENH, and (E) DECH.

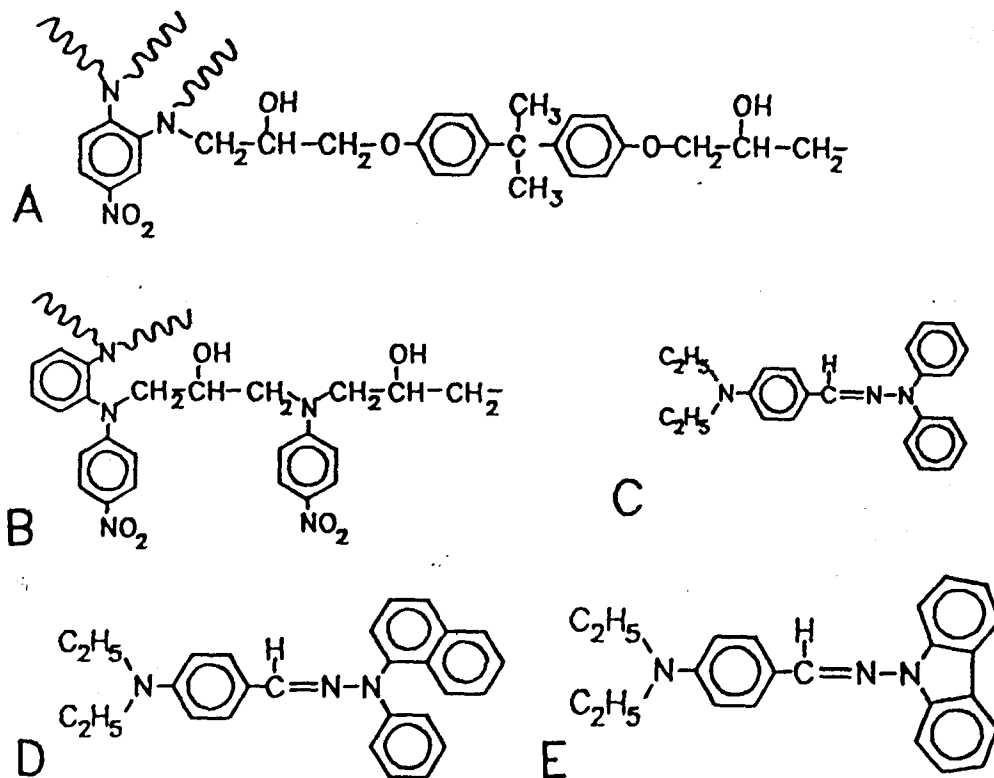


Fig. 3. Photoconductivity of bisA-NPDA/DEH expressed as a sensitivity, or conductivity change per unit intensity for both positive and negative charging as a function of wavelength.

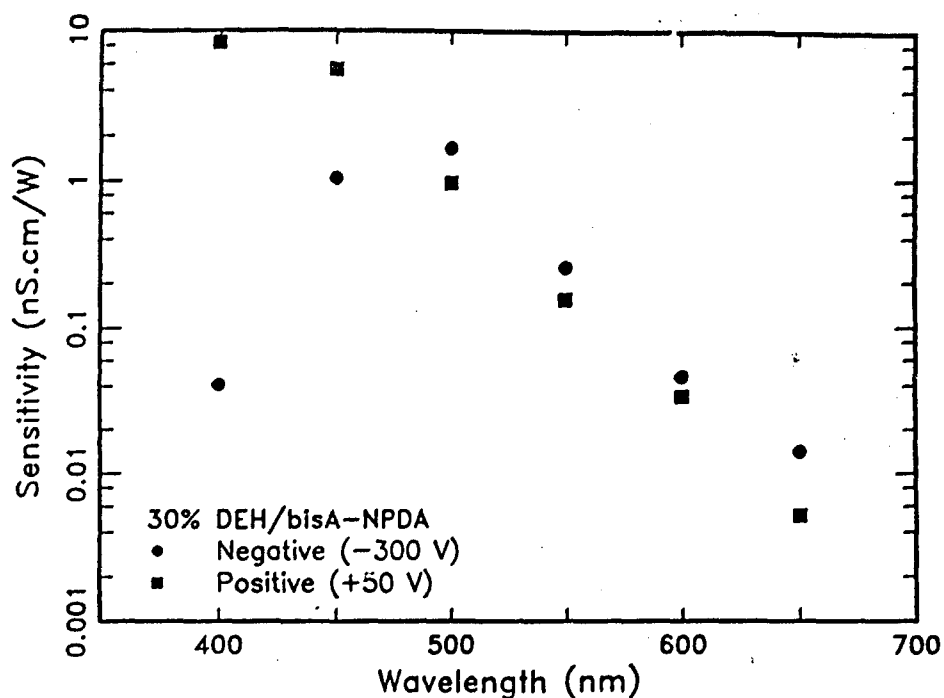


Fig. 4. Right ordinate: square of the electro-optic response ( $n^3 r_{\text{meas}}$ , with  $n$  the index of refraction) for p-polarized 632.8 nm radiation incident at an external angle of  $60^\circ$  on a  $356 \mu\text{m}$  thick film. Left ordinate: p-polarized diffraction efficiency at 647.1 nm for the same sample as a function of applied field. The inset shows the ratio of the latter to the former, which is proportional to  $r_{\text{eff}}$ .

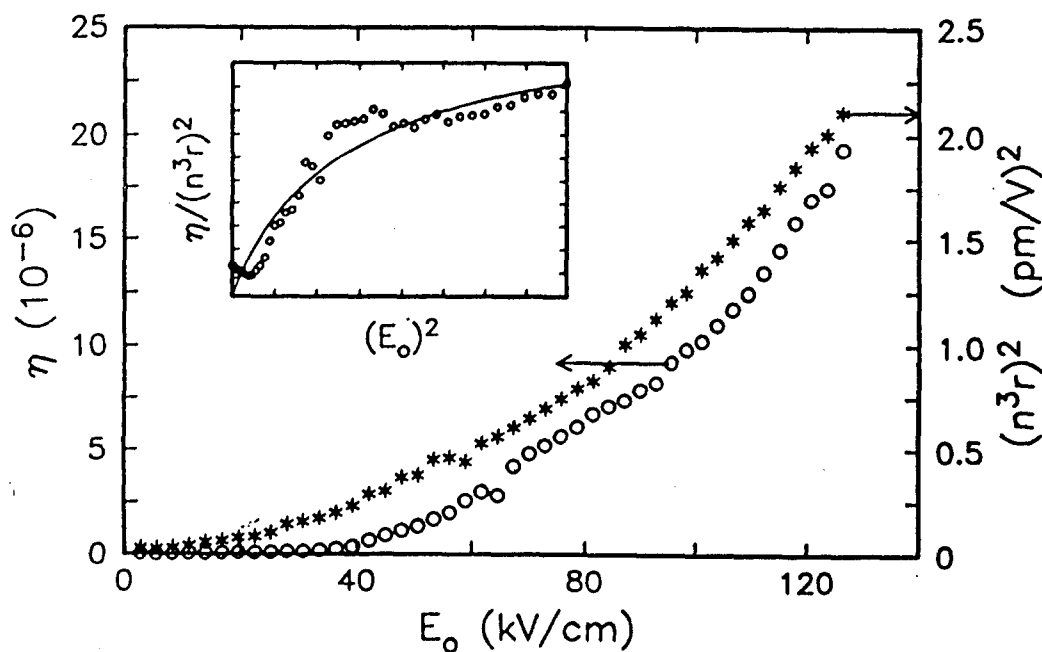


Fig. 5. Geometry for hologram recording. For definitions of the angles used, see text.

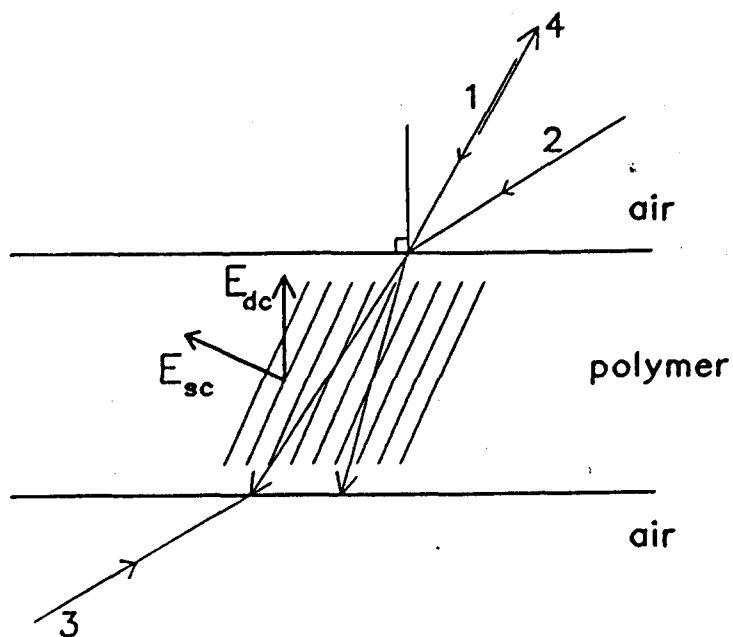


Fig. 6. Effect of applied field on grating readout by a weak reading beam: a-b) writing the grating in the presence of a (previously applied) negative voltage; b-c) writing beams and applied voltage turned off; c-d) positive voltage applied; d-e) negative voltage applied; e+) grating erasure by one strong beam.

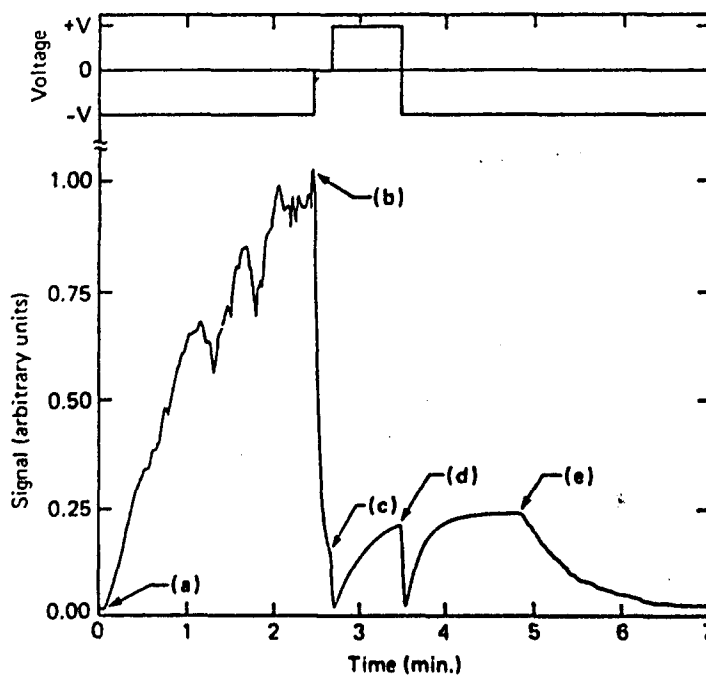


Fig. 7. Index grating phase versus field component along the grating wavevector. The solid curve is generated from Eq. (7), and the points are measured values for bisA-NPDA/DEIL.

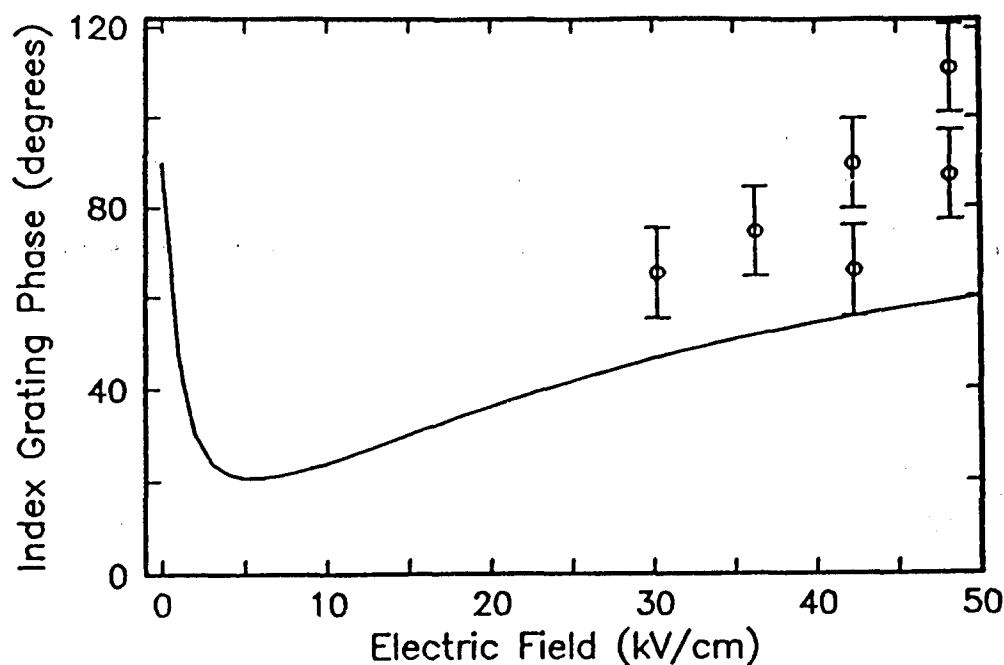
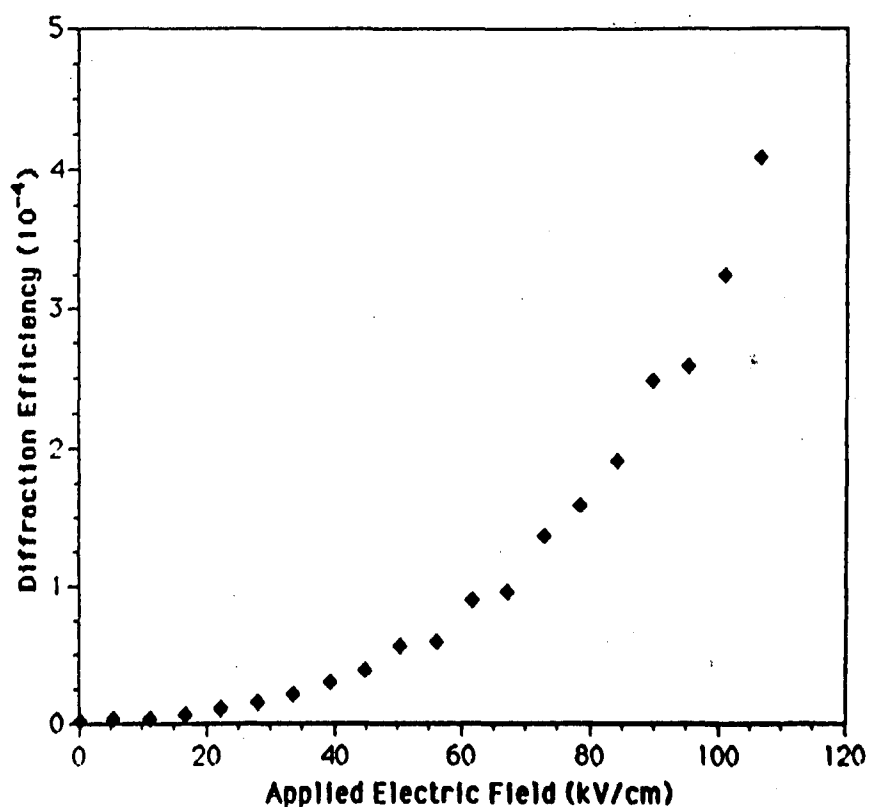


Fig. 8. Diffraction efficiency (steady-state) versus applied field for a 350  $\mu\text{m}$  sample of NNDN-NAN/25 wt. % DEIL.





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